



Experimental determination of the effective electrolyte conductivity in porous lead electrodes in the lead-acid battery

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Abstract—An electrochemical impedance technique which measures the impedance between two reference electrodes placed on opposite sides of the working electrode, and which can be used for the determination of the effective conductivity in the pore electrolyte in a porous electrode is presented. Information about the electroactive surface area and kinetic parameters can also be obtained from these measurements. A theoretical expression for the evaluation of the experimental results has been derived and analysed. The high frequency intercept of the impedance curve with the real axis will give the external ohmic resistance for electrode materials with an infinitely high conductivity. Even at very low frequencies, some of the current passing through the electrode will pass through the electrode in the solid material. The relative importance of this transfer of current in the solid phase through the electrode can be determined for the general case by the dimensionless quantity λ , which depends on the electrode thickness, the effective conductivity of the pore electrolyte and the local impedance. Two limiting cases can be observed. A comparison between this type of measurement and conventional electrochemical impedance spectroscopy measured between the working electrode and a reference electrode shows that the difference between the two methods depends on the relative magnitude of the local impedance. The method has been used for the evaluation of data for a porous lead electrode in the lead-acid battery system. The experimental data obtained at different states of discharge have been analysed by means of an impedance model, which takes into account the distribution of the local impedance in the porous structure, as well as the electrochemical reaction and mass transfer limitations in the electrode. Good agreement between the experimental data and the model has been obtained. © 1997 Elsevier Science Ltd. All rights reserved.

Key words: Porous electrode, lead electrode, lead-acid battery, electrochemical impedance spectroscopy, effective conductivity measurements.

INTRODUCTION

Porous electrodes have a wide field of applications, and are commonly used in batteries and fuel cells. The electrochemical performance of these electrodes is determined by a number of factors, *eg* the kinetics of the electrochemical reaction, the rate of mass transfer to the electrode surface and the current distribution in the electrode. The latter is determined to a large extent by the effective conductivities in the porous electrode matrix and in the pore electrolyte, which in turn depend on the structure and porosity of the battery electrode, and which will change during charge and discharge of the electrode. A further complication arises in a partly flooded fuel cell electrode, which has a three phase structure in order to give gaseous reactants and/or products access to the interior of the electrode. The effective ionic

conductivity will depend on the wetting of the surface and the electrolyte content, factors which may change during operation of the cell. Thus, in order to understand and optimize the performance of a porous electrode, it is important to know the effective conductivities both of the electrode matrix and in the pore electrolyte. Experimental techniques for determination of these parameters are significant.

Micka and Svata [1] presented a method for the evaluation of the tortuosity factor of a porous battery electrode by the determination of the effective conductivity of the pore electrolyte. They used a similar cell design to that used in this investigation and measured the potential drop over the electrode as a function of current density. This method was corrected for the screening effect of the reference capillaries. The potential transients of a battery

electrode after applying a current step were treated theoretically by Micka and Rousar [2], and measurements using this method on porous lead dioxide electrodes were presented by Calabek and Micka [3]. However, the method needs specially designed current collectors in the electrode and can not easily be utilized on standard electrodes.

In this paper an electrochemical impedance technique is presented, which can be used for determination of the effective conductivity of the pore electrolyte in a porous electrode. Information about the electroactive surface area and kinetic parameters can also be obtained from these measurements. The same type of measurement has been used on porous gas diffusion cathodes in the molten carbonate fuel cell system [4]. The technique is similar to that described by Atlung and Jacobsen [5] for the determination of kinetic properties of electroactive powders.

EXPERIMENTAL

Standard lead battery electrodes of 1.6 mm thickness from Tudor AB, Sweden, have been investigated. The principal experimental setup is shown in Fig. 1. The porous lead electrode was placed centrally in the plexiglas cell. Two Luggin capillaries connected to reference electrodes were placed a few mm from the external surface on each side of the

porous electrode. Two small fully charged porous lead electrodes in an electrolyte of the same composition as in the cell were used as reference electrodes. Compact lead sheets of a few mm thickness were used as counter electrodes. These were placed on each side of the working electrode. The electrolyte was 5 M H_2SO_4 , and the volume of the cell was large enough to ensure that the sulphuric acid concentration was kept within a few per cent variation during the cycling of the electrode. The electrode was preformed by a number of galvanostatic charge and discharge cycles at a current density of 16 A m^{-2} in order to obtain a reproducible and isotropic morphology of the porous electrode.

The electrochemical impedance spectra were measured under potentiostatic control at the open circuit potential difference between the two reference electrodes, which should be zero, by a Solartron 1286 Electrochemical Interface and a Solartron 1255 Frequency Response Analyser in the frequency range 6 kHz–6 mHz and an amplitude of 5 mV. Impedance spectra for different states of discharge were recorded. The electrode was slowly discharged from both sides at a current density of 16 A m^{-2} between the measurements. In order to remove concentration gradients in the electrode, it was allowed to rest for at least 1 h after the end of the discharge before the impedance spectra were recorded.

MODEL DESCRIPTION

Total impedance model for the porous electrode

The porous electrode consists of a solid matrix and an electrolyte which penetrates its pores. The structure of the electrode is assumed to be uniform. The electrode is regarded as pseudo-homogeneous, with the ionic conductivity in the pore electrolyte given by an effective conductivity, κ_{eff} . The one-dimensional current balance for the pore electrolyte is given by

$$\frac{\partial^2 \Phi}{\partial \xi^2} = \frac{L}{\kappa_{\text{eff}}} \frac{\partial j}{\partial \xi} \quad (1)$$

where j is the apparent current density in the electrolyte phase. L is the electrode thickness and ξ is the dimensionless electrode thickness defined as $\xi = x/L$.

Laplace transformation of the current balance for a small potential perturbation around the steady-state potential gives [6]

$$\frac{\partial^2 \bar{\Phi}}{\partial \xi^2} = \frac{L^2 \bar{\Phi}}{\kappa_{\text{eff}} z_{\text{loc}}} \quad (2)$$

where the bars indicate the Laplace transform of the perturbed potential. The local impedance, z_{loc} , depends on the Faradaic and non-Faradaic processes in the electrode, and is defined as

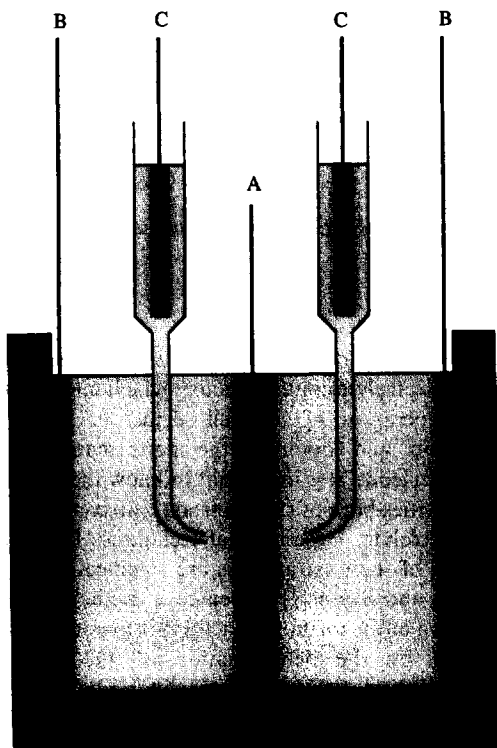


Fig. 1. Schematic of plexiglas cell used for conductivity measurements. A: Porous lead electrode; B: Counter electrodes of compact lead; C: Reference electrodes of porous lead.

$$z_{\text{loc}} = \frac{L\bar{\Phi}}{\frac{\partial j}{\partial \xi}} \quad (3)$$

This will be further described below. Since the amplitude of the potential perturbation is small, the local impedance is assumed to be independent of position in the electrode. Concentration gradients of sulphuric acid in the electrode are neglected, which makes the ionic conductivity independent of position as well.

In order to solve equation (2), two boundary conditions are needed. At the surface of the electrode

$$(\bar{\Phi})_{\xi=1/2} = \bar{\Phi}_0 \quad (4)$$

In the middle of the electrode, owing to symmetry

$$(\bar{\Phi})_{\xi=0} = 0 \quad (5)$$

The total impedance for one symmetric half of the electrode can be calculated analytically. The total impedance of the electrode is obtained by multiplying this result by two. The ohmic resistance of the electrolyte between the reference electrodes and the porous electrode on both sides, R_s , will also contribute to the impedance measured between the reference electrodes, which finally gives

$$Z_{\text{tot}} = R_s + 2\sqrt{\frac{z_{\text{loc}}}{\kappa_{\text{eff}}}} \tanh\left(\frac{L}{2\sqrt{z_{\text{loc}}\kappa_{\text{eff}}}}\right) \quad (6)$$

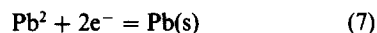
It is assumed that all physical properties are constant over the electrode. The total impedance for any partly or totally flooded porous electrode can be calculated by the insertion of an appropriate expression for the local impedance in the equation above. Equation (6) is equivalent to that obtained for a single particle by Atlung and Jacobsen [5], if the conductivity in the solid phase is assumed to be infinitely high. In their expression, L denotes the particle length instead of electrode thickness.

If the morphology and the porosity of the electrode is non-uniform, the local impedance and the effective ionic conductivity will depend on position and equation (6) will not be valid. This is the case if the electrode is discharged at a much higher rate, where the distribution of the electrochemical reaction rate in the porous electrode will result in a larger utilization of the material and thus a lower porosity at the outermost part of the electrode.

Local impedance model for the lead electrode

The discharge of a lead electrode in sulphuric acid leading to the formation of lead sulphate is believed to proceed through a discharge precipitation reaction, with the formation of dissolved lead ions at the interface followed by the diffusion of lead ions in the solution and the precipitation of lead sulphate somewhere in the electrode [7]. For the description of the local impedance in this model a quite simple model has been used. The mechanism has been

divided into two steps, the charge transfer reaction at the electrode



and the diffusion of Pb^{2+} ions in the electrolyte at the lead surface.

The Faradaic impedance for this mechanism then becomes

$$z_f = \frac{RT}{nFi_0} + \frac{RT}{n^2F^2C_{\text{Pb}^{2+}}\sqrt{D_{\text{Pb}^{2+}}}} \frac{1}{\sqrt{j\omega}} \quad (8)$$

where i_0 is the exchange current density for reaction [7], $C_{\text{Pb}^{2+}}$ is the concentration and $D_{\text{Pb}^{2+}}$ is the diffusion coefficient of dissolved lead ions. The first term on the right side of equation (8) can be identified as the charge transfer resistance, R_{ct} , and the second as the Warburg impedance, where the diffusion is assumed to be planar and not restricted in diffusion length.

If the double layer is assumed to be unaffected by the Faradaic reaction, the total local impedance of the porous electrode becomes

$$z_{\text{loc}} = \frac{1}{S}\left(\frac{1}{z_f} + j\omega C_{\text{dl}}\right)^{-1} \quad (9)$$

where C_{dl} is the double layer capacitance and S is the specific surface area of the electrode, j denotes the imaginary number and ω is the angular frequency. This expression for the local impedance can then be used for calculation of the total impedance of the porous electrode in equation (6).

Fitting of experimental data

The impedance model to be fitted can be expressed as

$$Z_{\text{calc}} = Z_{\text{calc}}(\omega, \mathbf{a}) \quad (10)$$

where $\mathbf{a}$ are the fitting parameters. The least square fitting involves minimizing the sum of squares merit function

$$\chi^2(\mathbf{a}) = \sum_{i=1}^k \left\{ \left[\frac{Z'_{\text{exp},i} - Z'_{\text{calc},i}}{\sigma_i} \right]^2 + \left[\frac{Z''_{\text{exp},i} - Z''_{\text{calc},i}}{\sigma_i} \right]^2 \right\} \quad (11)$$

where k is the number of data points. The standard deviation of each data point has been assumed to be proportional to the modulus of the impedance

$$\sigma_i = 0.005|Z_{\text{exp},i}| \quad (12)$$

which is given by the specification and settings of the Frequency Response Analyser. Actually, equation (11) implicates the use of weighted least square fitting, where the weight of each data point is inversely proportional to its standard deviation.

The measured data are subject to measurement errors. Thus, they will never exactly fit a model, even if the model is correct. In order to estimate the probability that the model is appropriate, the goodness-of-fit of the model can be statistically tested. This treatment of the merit function assumes that the measuring errors are normally distributed and that the standard deviation of each data point is known. The quantity Q gives the probability that the merit function exceeds a particular value by chance, and is calculated by means of the complement of the incomplete gamma function [8]. This treatment of the data will also provide the opportunity to calculate the standard deviation of the fitting parameters. It must, however, be assumed that the fitted model is correct.

THEORETICAL ANALYSIS

It might be of some general interest to look at the behaviour of equation (6) in order to examine the usefulness and limitations of the experimental technique described in this work for determination of the effective conductivity of the pore electrolyte as well as some kinetic parameters.

In the absence of Faradaic reactions

Let us first consider the case where the Faradaic impedance of the electrode is infinitely high, *i.e.* in the absence of any electrochemical charge transfer reaction. The local impedance will be due to the charging of the double layer, which gives the following expression for the local impedance

$$Z_{\text{loc}} = \frac{1}{j\omega C_{\text{dl}} S}. \quad (13)$$

Two limiting cases for the total impedance can be observed. At an infinitely high frequency, the local impedance will become infinitely small which in equation (6) gives

$$Z_{\text{tot}, \omega \rightarrow \infty} = R_s. \quad (14)$$

Thus, at high frequencies the current will pass through the electrode merely in the solid electrode matrix, which is assumed to have an infinitely high conductivity. The high-frequency intercept of the impedance curve with the real axis will give the external ohmic resistance.

The second limiting case is observed at low frequencies, when the local impedance becomes infinite, which in equation (6) gives

$$Z_{\text{tot}, \omega \rightarrow 0} = R_s + \frac{L}{\kappa_{\text{eff}}}. \quad (15)$$

This implies that all the current is passed through the pore electrolyte at low frequencies. The sum of the external resistance and the ratio of the electrode thickness to the effective ionic conductivity in the pore electrolyte can be determined from the low-frequency intercept of the curve with the real

axis. Subtraction of equation (14) from equation (15) shows that, if the electrode thickness is known, the effective conductivity of the pore electrolyte can be determined from the difference between the high frequency and low frequency intercept of the experimental curve with the real axis.

In the presence of Faradaic reactions

The presence of Faradaic reactions in the porous electrode will affect the total impedance of the electrode. At high frequencies the local impedance will be dominated by the double layer charging. For an infinitely high frequency, the local impedance behaves as in the absence of any Faradaic reactions and it becomes infinitely large, which consequently gives a total impedance according to equation (14).

The influence of the charging of the double layer is less pronounced at lower frequencies, since the impedance caused by the double layer will be inversely proportional to the frequency. For the simple case with a pure charge transfer reaction without any mass transfer limitations, the charge transfer resistance will be constant and will show no frequency dependence. It can then be seen that some of the current passing through the electrode will be transferred between the electrolyte and the electrode matrix by the electrochemical reaction and will pass through the electrode in the solid material, even at very low frequencies. The amount of current passing through the electrode material depends on the relative magnitude of the charge transfer resistance. The relative importance of this transfer of current in the solid phase through the electrode can be determined for the general case by the dimensionless quantity

$$\lambda = \frac{L}{2\sqrt{Z_{\text{loc}} \kappa_{\text{eff}}}}. \quad (16)$$

Two limiting cases can be observed. If λ becomes small owing to a relatively large local impedance, $\tanh(\lambda)/\lambda$ will become close to one, and the total impedance measured over the electrode becomes

$$Z_{\text{tot}, \lambda \rightarrow 0} = R_s + \frac{L}{\kappa_{\text{eff}}} \quad (17)$$

which is the same relation that is obtained at low frequencies in the absence of any Faradaic reactions, equation (15). The total impedance will be determined by the external resistance, the electrode thickness and the effective conductivity of the pore electrolyte. The influence of current passing through the electrode in the solid material can then be neglected.

For large values of λ , $\tanh(\lambda)$ will become close to one, and equation (6) gives

$$Z_{\text{tot}, \lambda \rightarrow \infty} = R_s + 2\sqrt{\frac{Z_{\text{loc}}}{\kappa_{\text{eff}}}} \quad (18)$$

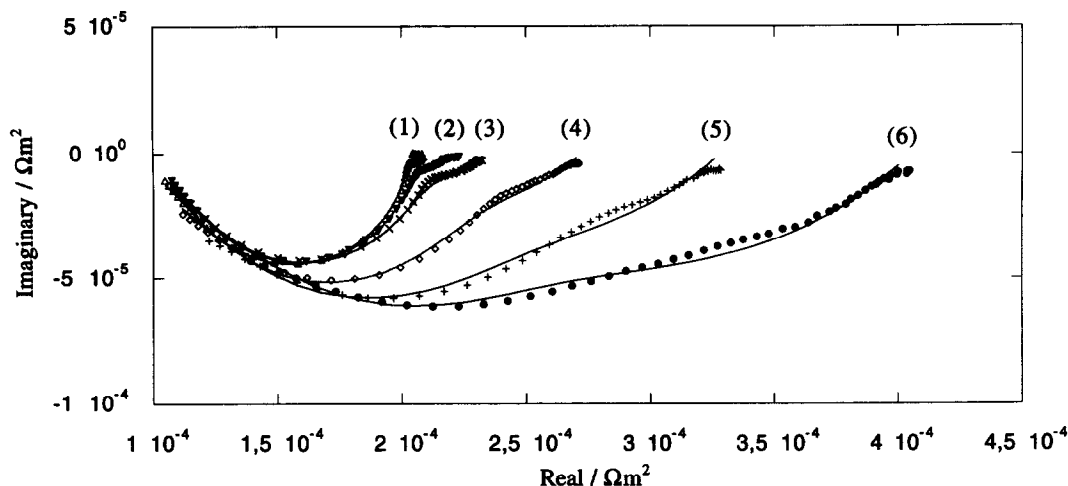


Fig. 2. Electrochemical impedance spectra of a lead electrode in 5 M H₂SO₄ for different states of discharge. (1) 0 Ahm⁻² (2) 28.6 Ahm⁻² (3) 138 Ahm⁻² (4) 272 Ahm⁻² (5) 413 Ahm⁻² (6) 530 Ahm⁻². Data points: Experimental results. Solid line: Theoretical model fitted to experimental data. For values of fitted parameters, see Table 1.

The total impedance will then be determined by the external resistance, the local Faradaic impedance, z_{loc} , and the effective conductivity of the pore electrolyte. It is worth noting that the thickness of the electrode will have no impact on the result. For determination of the effective conductivity in this case, the local impedance must be known.

A comparison to conventional measurements of the impedance of porous electrodes

It is interesting to see how the results obtained by this method are related to the results obtained by conventional electrochemical impedance spectroscopy of porous electrodes. If the impedance is measured in the same type of cell in a conventional way, *ie* between the working electrode and a reference electrode, and not between two reference electrodes placed on each side of the unconnected working electrode, the total impedance becomes [6]

$$Z_{tot} = R'_s + \sqrt{\frac{z_{loc}}{\kappa_{eff}}} \coth\left(\frac{L}{2\sqrt{z_{loc}\kappa_{eff}}}\right). \quad (19)$$

It is assumed that the counter electrodes are placed at equal distances on each side of the working electrode.

Two limiting cases can be observed also for this type of measurement. If λ is small, $\lambda \coth(\lambda)$ will become close to one, and the total impedance of the electrode becomes

$$Z_{tot, \lambda \rightarrow 0} = R'_s + \frac{2z_{loc}}{L}. \quad (20)$$

The result shows that the electrode in this case will behave as a flat electrode, and the result will be independent of the effective conductivity of

the pore electrolyte, which therefore cannot be determined.

For large values of λ , $\coth(\lambda)$ will become close to one, which gives

$$Z_{tot, \xi \rightarrow \infty} = R'_s + \sqrt{\frac{z_{loc}}{\kappa_{eff}}}. \quad (21)$$

This is, in principle, the same result that will be obtained from the conductivity measurements for large values of λ , equation (18). Thus, in this case the same information will be obtained from both types of measurements.

It can be concluded that a major difference between the two methods can be observed for small values of λ , where the conventional measurements will provide information about the local impedance, while the conductivity measurements will give information about the effective conductivity of the pore electrolyte. Thus, in this case and in the intermediate region, *ie* $0.2 < \lambda < 3$, the two methods will give different types of information and will be a complement to each other. For larger values of γ , the same information will be obtained from both methods. In the case of conductivity measurements, kinetic information about the porous electrode can be obtained without any electrical connection to this electrode.

In comparison to *dc*-measurements of the effective conductivity, there are some advantages of using electrochemical impedance spectroscopy. Both techniques will provide a value of the effective conductivity. However, since the impedance measurements also provide kinetic information, it is possible to estimate the relative importance of the transfer of current in the solid phase on the determined conductivity value in this case.

Table 1.
Fitted parameters for a lead electrode at different states of discharge

Sample no.	1	2	3	4	5	6
Depth of discharge/Ah m^{-2}	0	28.6	138	272	413	530
χ^2	69.95	54.63	46.89	88.76	198.6	157.8
Q	0.9826	0.9998	0.9999	0.7127	5.67e-09	5.569e-05

RESULTS AND DISCUSSION

The experimental impedance data, as well as the fitted calculated curves for different state of discharge for a porous lead electrode, are shown in Fig. 2. The fitting parameters and the calculated square sums are shown in Table 1. The model gives very good fits of the experimental data for the fully and partly discharged electrode (Fig. 2, curves 1–4), whereas the fits for the almost fully discharged electrode is somewhat less good (Fig. 2, curves 5–6).

Effective conductivities

The discharge process in the lead electrode transforms lead into lead sulphate. The lead sulphate has a larger molar volume than the lead, which leads to a gradual plugging of the pores in the porous electrode during discharge of the electrode. The effective ionic conductivities obtained from the fitting of the model to the experimental impedance data as a function of state of charge are shown in Fig. 3. The results are somewhat lower but in fair agreement with the results obtained by Ekdunge and Simonsson [9] using *dc* measurements. The curve in the figure has been fitted to the experimental conductivity data by the Bruggeman equation

$$\kappa = \kappa_0 \left(\frac{\epsilon}{\epsilon_0} \right)^{1.5} \tag{22}$$

where κ_0 and ϵ_0 are the effective conductivity and porosity, respectively, in the fully charged electrode, and ϵ is the porosity of the electrode which is a linear

function of the state of discharge because of the difference in molar volume of lead and lead sulphate. The fit gives an effective conductivity of $13.6 \, \Omega^{-1} \text{m}^{-1}$ for the fully charged electrode.

As an alternative evaluation method, it is possible to estimate the effective conductivities graphically from the impedance curves, as has already been discussed above. If some of the current passes through the electrode in the solid material, this method will result in an overestimation of the conductivity. The results from the much simpler graphical method and those from the fitting procedure of the experimental data for this electrode are in good agreement, which indicates that the amount of current passing through the solid phase at low frequencies is very small.

Specific surface area

During the discharge of the porous electrode the formation of lead sulphate will result in a gradual blocking of the lead surface. The specific surface area of the lead in the porous electrode can be determined indirectly from the distributed capacitance. If the double layer capacitance based on actual surface area of lead is assumed to be independent of the state of discharge, and the lead sulphate can be treated as an isolator, the difference in capacitance will be due to changes in electroactive surface area of the lead. In these calculations the double layer capacitance based on actual surface area has been fixed at 0.2 F m^{-2} . The results show a gradual decrease in electroactive surface area, see Fig. 4, as could be expected.

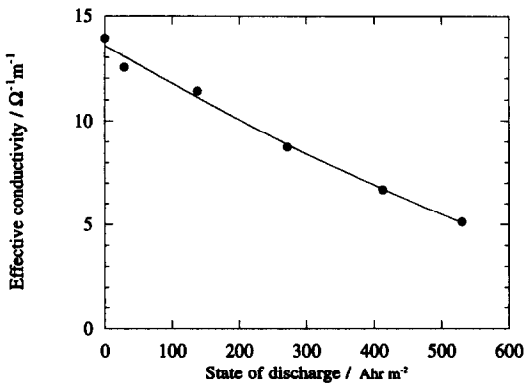


Fig. 3. Effective conductivity as a function of state of discharge for a lead electrode in 5 M H_2SO_4 . Solid line: Experimental data fitted to equation (22).

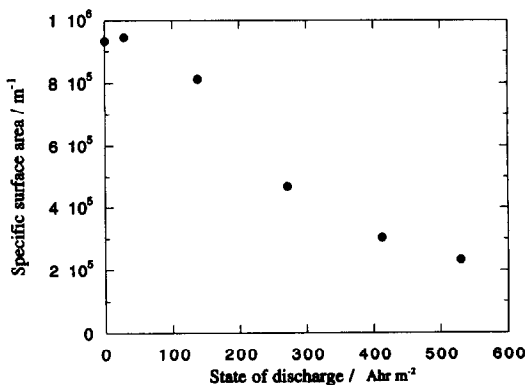


Fig. 4. Specific surface area of lead as a function of state of discharge for a lead electrode in 5 M H_2SO_4 .

Kinetic parameters

Under certain conditions, as has already been discussed, this type of conductivity measurement can provide kinetic information. The kinetic model used includes a charge transfer resistance due to the electrochemical reaction and a Warburg impedance caused by the diffusion of dissolved lead ions in the electrolyte. In the fitting procedure these parameters are based on the electroactive surface area of lead, as determined from the capacitance.

The charge transfer resistance is in the range of $0.18\text{--}0.006\ \Omega\ \text{m}^2$, see Fig. 5. From equation (8) it can be seen that the exchange current density can be calculated from the charge transfer resistance according to the equation

$$i_0 = \frac{RT}{nFR_{ct}} \quad (23)$$

The exchange current density falls in the range of $0.07\text{--}2\ \text{A}\ \text{m}^{-2}$. This is in fair agreement with the literature data obtained from the charging of porous lead electrodes which are of the order of $0.1\ \text{A}\ \text{m}^{-2}$ [7]. The exchange current density based on electrode volume is in the range of $0.7 \times 10^5\text{--}5 \times 10^5\ \text{A}\ \text{m}^{-3}$, which is in reasonable agreement with literature data [9].

The combined effect of the concentration and diffusivity of dissolved Pb^{2+} can be determined from the Warburg coefficient σ , Fig. 6, which according to equation (8) gives

$$C_{\text{Pb}^{2+}} \sqrt{D_{\text{Pb}^{2+}}} = \frac{RT}{n^2 F^2 \sigma} \quad (24)$$

This results in a $CD^{1/2}$ value for Pb^{2+} in the range of $1.1 \times 10^{-7}\text{--}6.8 \times 10^{-7}\ \text{mol}\ \text{m}^{-2}\ \text{s}^{1/2}$. Literature data give a solubility of Pb^{2+} of $4.4 \times 10^{-6}\ \text{M}$ and a diffusion coefficient of $0.23 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$ in $5\ \text{M}\ \text{H}_2\text{SO}_4$ at 20°C [10], which gives a $CD^{1/2}$ of $6.7 \times 10^{-8}\ \text{mol}\ \text{m}^{-2}\ \text{s}^{1/2}$. This is somewhat lower than the data obtained in this work.

The exchange current density and consequently the charge transfer resistance as well as the concentration and diffusivity of lead ions would be expected to be

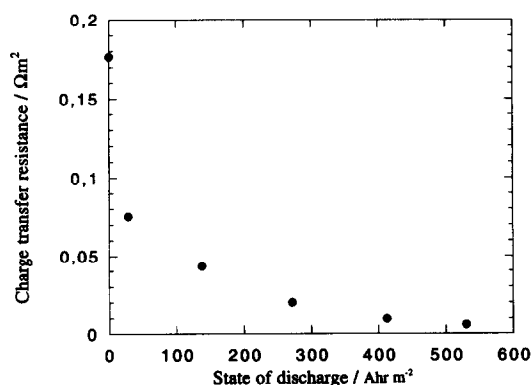


Fig. 5. Charge transfer resistance as a function of state of discharge for a lead electrode in $5\ \text{M}\ \text{H}_2\text{SO}_4$.

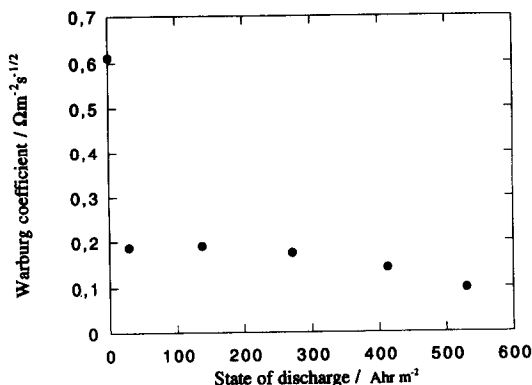


Fig. 6. Warburg coefficient as a function of state of discharge for a lead electrode in $5\ \text{M}\ \text{H}_2\text{SO}_4$.

constant and independent of state of discharged. The variation is not too large and all the data fall within the same order of magnitude. The method can at least be used for an order of magnitude estimation of kinetic data. The deviation of the kinetic data for the fully charged electrode can be attributed to the small influence of the Faradaic reaction in this case, and thus a very uncertain determination of the kinetic parameters. The decrease of the charge transfer resistance as a function of state of discharge may be due to the formation of a barrier layer of lead sulphate on the lead surface [11]. This could further explain why the experimental data for a discharge electrode fit the model less well.

CONCLUSIONS

An electrochemical impedance technique has been presented, which can be used for determination of the effective conductivity of the pore electrolyte in a porous electrode. Information about the electroactive surface area and kinetic parameters can also be obtained from these measurements. A theoretical expression for evaluation of the experimental results has been derived.

Analysis of the theoretical expression shows that at high frequencies the current will pass through the electrode merely in the solid electrode matrix which is assumed to have an infinitely high conductivity. The high-frequency intercept of the impedance curve with the real axis will give the external ohmic resistance. Even at very low frequencies, some of the current passing through the electrode will be conducted in the solid material. The relative importance of this transfer of current in the solid phase through the electrode can be determined for the general case by the dimensionless quantity λ , given by equation (16). Two limiting cases can be observed. If λ becomes small due to a relatively large local impedance, the total impedance will be determined by the external resistance, the electrode thickness and the effective conductivity of the pore electrolyte. The influence of current passing through the electrode in

the solid material can then be neglected. For large values of λ , the total impedance will be determined by the external resistance, the local Faradaic impedance and the effective conductivity of the pore electrolyte.

A comparison between this type of measurement and conventional electrochemical impedance spectroscopy shows that a major difference between the two methods can be observed for small values of λ , where the conventional measurements will provide information about the local impedance, while the conductivity measurements will give information about the effective conductivity in the pore electrolyte. Thus, in this case and in the intermediate region, the two methods will complement each other. For large values of λ , the same information will be obtained from both methods.

The method has been used for the evaluation of data for a porous lead electrode in the lead-acid battery system. The experimental data obtained at different states of discharge have been analysed by means of an impedance model, which takes into account the distribution of the local impedance in the porous structure, as well as the electrochemical reaction and mass transfer limitations in the electrode. Kinetic parameters have been obtained by fitting this model to the experimental data. Good agreement between the experimental data and the model has been obtained. The obtained values for the effective conductivities in the pore electrolyte are reasonable. The surface area, exchange current

density and mass transfer parameters for lead ions are in reasonable agreement with literature data.

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